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INTRODUCTION

The number of chemical agents used in a production, research, patient care or teaching facility is large, too large, to provide for agent-specific guides. However, there are general criteria that can be used to protect not only the operator of a chemical activity but also coworkers and ultimately the general public. This guide is intended to be used as a source of information, teaching tool, as well as a reference to follow generally acceptable rules governing the safety of chemical operations.

Much has been learned from accidents, some minor others major, on properties of chemicals and how to manage, and more importantly, how not to manage, a chemical operation. Prior to the development of the instrumental or other rapid methods to identify chemical agents taste and smell were primary methods for identification of chemicals. Among all early investigators, Karl Wilhelm von Scheele, the eighteenth century Swedish chemist is credited with having established the taste and smell of many chemicals known at that time. Although the odor of many chemicals is specific and characteristic, the availability of highly sensitive and substance specific analytical methods, smell and taste are no longer reasonable detection techniques. Today's safety requirements prohibits the usage of taste and smell because of potential adverse toxic effects as a consequence of inhalation or ingestion of many chemicals routinely used in the laboratory.

This Chemical Hygiene Guide is adopted from several sources. Much of the text is taken from several reports of the National Research Council, the research arm of the National Academy of Sciences, National Academy of Engineering, and Institute of Medicine located in Washington, DC. Other sources of information include the following:

- Various regulations of the Occupational Safety and Health Administration (OSHA) and those of the U.S. Environmental Protection Agency (EPA).
- Publications of International Agency for Research of Cancer (IARC)
- International Standardization Organization(ISO), and the American National Standards Institute, the U. S counterpart to ISO.

The Chemical Hygiene Guide is not intended to be a replacement for legal mandates. ICESH uses policies to cover these mandates. Instead this guide should be used a tool to comply with the legal mandates. Whereas legal mandates are likely to deviate from one country to another one, guides are based on generally accepted safety principles and are likely to be generally applicable. Much like other scientific information, chemical hygiene is subject to development, advancement and change. Accordingly, this guide will be revised as necessary.

GENERAL PRINCIPLES

Each chemical agent and every chemical reaction are unique and require attention to their safety requirements. The exact number of chemicals available in commerce and routinely used is unknown. Consequently, it is impossible to design a set of rules that will cover all possible hazards and occurrences for each chemical. Instead a properly managed chemical operation relies upon general guidelines based on general scientific principles, application of basic chemistry to specific situations, and experience including mishaps of varying severity.

The rule governing chemical hygiene are similar to those for most other operations. There are nine rules governing most if not all activities of chemical operations:

ICESH Rule I: *Safety must be the second objective of every operation*

The primary objective of every operation is the accomplishment of its stated objective. For example, the primary objective of a facility that is designed to produce a specific chemical is the production. Similarly, the objective of an investigator may be to synthesize a chemical, analyze a mixture, or evaluate a chemical reaction. However, all of these and all other activities that involve chemical must accept safety as their secondary objective. The literature is littered with failed attempts to accomplish a task because safety requirements were not appropriately considered and accommodated.

ICESH Rule II: Unambiguous Custodians must be appointed for each operation including its subparts.

ICESH Rule III: All activities that may enhance the intake of chemicals via ingestion, inhalation, or skin absorption must be prohibited in a chemical operation.

ICESH Rule IV preplanning

ICESH Rule V pressure, temp

ICESH Rule VI Protective

ICESH Rule VII facilities

ICESH Rule VIII Emergency Equipment

ICESH Rule IX Training

are

The most important rule is that everyone involved in laboratory operations--from the highest administrative level to the individual worker--must be safety minded. Safety awareness can become part of everyone's habits only if the issue of safety is discussed repeatedly and only if senior and responsible staff evince a sincere and continuing interest and are perceived by all their associates as doing so. The individual, however, must accept responsibility for carrying out his or her own work in accordance with good safety practices and should be prepared in advance for possible accidents by knowing what emergency aids are available and how they are to be used.

The supervisor of the laboratory has overall safety responsibility and should provide for regular formal safety and housekeeping inspections (at least quarterly for universities and other organizations that have frequent personnel changes and semiannually for other laboratories) in addition to Continual informal inspections. Laboratory supervisors have the responsibility of ensuring that (a) workers know safety rules and follow them, (b) adequate emergency equipment in proper working order is available, (c) training in the use of emergency equipment has been provided, (d) information on special or unusual hazards in

non-routine work has been distributed to the laboratory workers, and (e) an appropriate safety orientation has been given to individuals when they are first assigned to a laboratory space.

The laboratory worker should develop good personal safety habits: (a) eye protection should be worn at all times, (b) exposure to chemicals should be kept to a minimum, and (c) smoking and eating must be avoided in areas where chemicals are present.

Advance planning is one of the best ways to avoid serious incidents. Before performing any chemical operation, the laboratory worker should consider "What would happen if . . ." and be prepared to take proper emergency actions.

Over familiarity with a particular laboratory operation may result in overlooking or underrating its hazards. This attitude can lead to a false sense of security, which frequently results in carelessness. Every laboratory worker has a basic responsibility to himself or herself and colleagues to plan and execute laboratory operations in a safe manner.

Every laboratory worker should observe the following rules:

1. Know the safety rules and procedures that apply to the work that is being done. Determine the potential hazards (e.g., physical, chemical, biological) (see Chapters I.B-D) and appropriate safety precautions before beginning any new operation.
2. Know the location of and how to use the emergency equipment in your area, as well as how to obtain additional help in an emergency, and be familiar with emergency procedures.
3. Know the types of protective equipment available and use the proper type for each job.
4. Be alert to unsafe conditions and actions and call attention to them so that corrections can be made as soon as possible. Someone else's accident can be as dangerous to you as any you might have.
5. Avoid consuming food or beverages or smoking in areas where chemicals are being used or stored.
6. Avoid hazards to the environment by following accepted waste disposal procedures. Chemical reactions may require traps or scrubbing devices to prevent the escape of toxic substances.
7. Be certain all chemicals are correctly and clearly labeled. Post warning signs when unusual hazards, such as radiation, laser operations, flammable materials, biological hazards, or other special problems exist.
8. Remain out of the area of a fire or personal injury unless it is your (General Recommendations for Safe Practices in Laboratories) responsibility to help meet the emergency. Curious bystanders interfere with rescue and emergency personnel and endanger themselves.
9. Avoid distracting or startling any other worker. Practical jokes or horseplay cannot be tolerated at any time.
10. Use equipment only for its designed purpose.

11. Position and clamp reaction apparatus thoughtfully in order to permit manipulation without the need to move the apparatus until the entire reaction is completed. Combine reagents in appropriate order, and avoid adding solids to hot liquids.
12. Think, act, and encourage safety until it becomes a habit.

HEALTH AND HYGIENE

Laboratory workers should observe the following health practices:

1. Wear appropriate eye protection at all times.
2. Use protective apparel, including face shields, gloves, and other special clothing or footwear as needed.
3. Confine long hair and loose clothing when in the laboratory.
4. Do not use mouth suction to pipet chemicals or to start a siphon; a pipet bulb or an aspirator should be used to provide vacuum.
5. Avoid exposure to gases, vapors, and aerosols. Use appropriate safety equipment whenever such exposure is likely.
6. Wash well before leaving the laboratory area. However, avoid the use of solvents for washing the skin. They remove the natural protective oils from the skin and can cause irritation and inflammation. In some cases, washing with a solvent might facilitate absorption of a toxic chemical.

FOOD HANDLING

Contamination of food, drink, and smoking materials is a potential route for exposure to toxic substances. Food should be stored, handled, and consumed in an area free of hazardous substances.

1. Well-defined areas should be established for storage and consumption of food and beverages. No food should be stored or consumed outside of this area.
2. Areas where food is permitted should be prominently marked and a warning sign (e.g., EATING AREA--NO CHEMICALS) posted. No chemicals or chemical equipment should be allowed in such areas.
3. Consumption of food or beverages and smoking must not be permitted in areas where laboratory operations are being carried out.
4. Glassware or utensils that have been used for laboratory operations should never be used to prepare or consume food or beverages. Laboratory refrigerators, ice chests, cold rooms, and such

should not be used for food storage; separate equipment should be dedicated to that use and prominently labeled.

HOUSEKEEPING

There is a definite relationship between safety performance and orderliness in the laboratory. When housekeeping standards fall, safety performance inevitably deteriorates. The work area should be kept clean, and chemicals and equipment should be properly labeled and stored.

1. Work areas should be kept clean and free from obstructions. Cleanup should follow the completion of any operation or at the end of each day.
2. Wastes should be deposited in appropriate receptacles.
3. Spilled chemicals should be cleaned up immediately and disposed of properly. Temple University has established disposal procedures for disposal of chemical waste and prompt laboratory accidents clean up.
4. Unlabeled containers and chemical wastes should be disposed of promptly, by using appropriate procedures. Such materials, as well as chemicals that are no longer needed, should not accumulate in the laboratory.
5. Floors should be cleaned regularly; accumulated dust, chromatography adsorbents, and other assorted chemicals pose respiratory hazards.
6. Equipment and chemicals should be stored properly; clutter should be minimized.

EQUIPMENT MAINTENANCE

Good equipment maintenance is important for safe, efficient operations. Equipment should be inspected and maintained regularly. Servicing schedules will depend on both the possibilities and the consequences of failure. Maintenance plans should include a procedure to ensure that a device that is out of service cannot be restarted.

GUARDING FOR SAFETY

All mechanical equipment should be adequately furnished with guards that prevent access to electrical connections or moving parts (such as the belts and pulleys of a vacuum pump). Each laboratory worker should inspect equipment before using it to ensure that the guards are in place and functioning.

Careful design of guards is vital. An ineffective guard can be worse than none at all, because it can give a false sense of security. Emergency shutoff devices may be needed, in addition to electrical and mechanical guarding.

SHIELDING FOR SAFETY

Safety shielding should be used for any operation having the potential for explosion such as (a) whenever a reaction is attempted for the first time (small quantities of reactants should be used to minimize hazards), (b) whenever a familiar reaction is carried out on a larger than usual scale (e.g., 5-10 times more material), and (c) whenever operations are carried out under non-ambient conditions. Shields must be placed so that all personnel in the area are protected from hazard.

GLASSWARE

Accidents involving glassware are a leading cause of laboratory injuries.

1. Careful handling and storage procedures should be used to avoid damaging glassware. Damaged items should be discarded or repaired.
2. Adequate hand protection should be used when inserting glass tubing into rubber stoppers or corks or when placing rubber tubing on glass hose connections. Tubing should be fire polished or rounded and lubricated, and hands should be held close together to limit movement of glass should fracture occur. The use of plastic or metal connectors should be considered.
3. Glass-blowing operations should not be attempted unless proper annealing facilities are available.
4. Vacuum jacketed glass apparatus should be handled with extreme care to prevent implosions. Equipment such as Dewar flasks should be taped or shielded. Only glassware designed for vacuum work should be used for that purpose.
5. Hand protection should be used when picking up broken glass. (Small pieces should be swept up with a brush into a dustpan.)
6. Proper instruction should be provided in the use of glass equipment designed for specialized tasks, which can represent unusual risks for the first-time user. (For example, separatory funnels containing volatile solvents can develop considerable pressure during use.)

FLAMMABILITY HAZARDS

Because flammable materials are widely used in laboratory operations, the following rules should be observed:

1. Do not use an open flame to heat a flammable liquid or to carry out a distillation under reduced pressure.
2. Use an open flame only when necessary and extinguish it when it is no longer actually needed.
3. Before lighting a flame, remove all flammable substances from the immediate area. Check all containers of flammable materials in the area to ensure that they are tightly closed.
4. Notify other occupants of the laboratory in advance of lighting a flame.

5. Store flammable materials properly.
6. When volatile flammable materials may be present, use only non-sparking electrical equipment.

COLD TRAPS AND CRYOGENIC HAZARDS

The primary hazard of cryogenic materials is their extreme coldness. They, and surfaces they cool, can cause severe burns if allowed to contact the skin. Gloves and a face shield may be needed when preparing or using some cold baths. Neither liquid nitrogen nor liquid air should be used to cool a flammable mixture in the presence of air because oxygen can condense from the air, which leads to an explosion hazard. Appropriate dry gloves should be used when handling dry ice, which should be added slowly to the liquid portion of the cooling bath to avoid foaming over. Workers should avoid lowering their head into a dry ice chest: carbon dioxide is heavier than air, and suffocation can result.

SYSTEMS UNDER PRESSURE

Reactions should never be carried out in, nor heat applied to, an apparatus that is a closed system unless it is designed and tested to withstand pressure. Pressurized apparatus should have an appropriate relief device. If the reaction cannot be opened directly to the air, an inert gas purge and bubbler system should be used to avoid pressure buildup.

WARNING SIGNS AND LABELS

Laboratory areas that have special or unusual hazards should be posted with warning signs. Standard signs and symbols have been established for a number of special situations, such as radioactivity hazards, biological hazards, fire hazards, and laser operations. Other signs should be posted to show the locations of safety showers, eyewash stations, exits, and fire extinguishers. Extinguishers should be labeled to show the type of fire for which they are intended. Waste containers should be labeled for the type of waste that can be safely deposited.

The safety- and hazard-sign systems in the laboratory should enable a person unfamiliar with the usual routine of the laboratory to escape in an emergency (or help combat it, if appropriate).

When possible, labels on containers of chemicals should contain information on the hazards associated with use of the chemical. Unlabeled bottles of chemicals should not be opened; such materials should be disposed of promptly and will require special handling procedures.

UNATTENDED OPERATIONS

Frequently, laboratory operations are carried out continuously or overnight. It is essential to plan for interruptions in utility services such as electricity, water, and inert gas. Operations should be designed to be safe, and plans should be made to avoid hazards in case of failure. Wherever possible, arrangements for routine inspection of the operation should be made and, in all cases, the laboratory lights should be left on and an appropriate sign should be placed on the door.

One particular hazard frequently encountered is failure of cooling water supplies. A variety of commercial or homemade devices can be used that (a) automatically regulate water pressure to avoid surges that might rupture the water lines or (b) monitor the water flow so that its failure will automatically turn off electrical connections and water supply valves.

WORKING ALONE

Generally, it is prudent to avoid working in a laboratory building alone. Under normal working conditions, arrangements should be made between individuals working in separate laboratories outside of working hours to crosscheck periodically. Alternatively, security guards may be asked to check on the laboratory worker. Experiments known to be hazardous should not be undertaken by a worker who is alone in a laboratory.

Under unusual conditions, special rules may be necessary. The supervisor of the laboratory has the responsibility for determining whether the work requires special safety precautions, such as having two persons in the same room during a particular operation.

ACCIDENT REPORTING

Emergency telephone numbers to be called in the event of fire, accident, flood, or hazardous chemical spill are posted prominently in each laboratory. In addition, the numbers of the laboratory workers and their supervisors should be posted. These persons should be notified immediately in the event of an accident or emergency.

EVERYDAY HAZARDS

Finally, laboratory workers should remember that injuries can and do occur outside the laboratory or other work area. It is important that safety be practiced in offices, stairways, corridors, and other places. Here, safety is largely a matter of common sense, but a constant safety awareness of everyday hazards is vital.

III. LABORATORY SAFETY PROCEDURES

A variety of specialized clothing and equipment is commercially available for use in the laboratory. The proper use of these items will minimize or eliminate exposure to the hazards associated with many laboratory operations. The primary goal of laboratory safety procedures is the prevention of accidents and emergencies. However, accidents and emergencies may nonetheless occur and, at such times, proper safety equipment and correct emergency procedures can help minimize injuries or damage.

Every laboratory worker should be familiar with the location and proper use of the available protective apparel and safety equipment and with emergency procedures. Instruction on the proper use of such equipment, emergency procedures, and first aid is available at Temple University to everyone who might need it.

GENERAL EYE PROTECTION POLICY

Eye protection is required for all personnel and any visitors present in locations where chemicals are stored or handled. No one should enter any laboratory without appropriate eye protection.

Conference rooms, libraries, offices, microscope rooms in which chemicals are not in use, and similar rooms are not normally eye protection areas. However, at any time when chemicals are used in such rooms, even temporarily, signs should be posted and all persons in the vicinity warned that eye protection is temporarily required. For laboratory operations that do not involve the use of chemicals and, if chemicals are not used in the immediate vicinity, it may be permissible by arrangement with the laboratory custodian, to remove the eye protection.

Safety spectacles that meet the criteria described below provide minimum eye protection for regular use. Additional protection may be required when carrying out more hazardous operations.

Laboratory custodians should make appropriate eye protection devices available to visitors or others who only occasionally enter eye protection areas. These devices would be used only on a temporary basis while the person is in the eye protection area. (For example, it may be useful to place a container of inexpensive safety glasses next to the entrance to each laboratory for use by visitors.) Contact lenses should not be worn in a laboratory. Gases and vapors can be concentrated under such lenses and cause permanent eye damage. Furthermore, in the event of a chemical splash into an eye, it is often nearly impossible to remove the contact lens to irrigate the eye because of involuntary spasm of the eyelid. Persons attempting to irrigate the eyes of an unconscious victim may not be aware of the presence of contact lenses, thus reducing the effectiveness of such treatment. Soft lenses can absorb solvent vapors even through face shields and, as a result, adhere to the eye.

There are some exceptional situations in which contact lenses must be worn for therapeutic reasons. Persons who must wear contact lenses should inform the laboratory custodian so that satisfactory safety precautions can be devised.

SAFETY SPECTACLES

Ordinary prescription glasses do not provide adequate protection from injury to the eyes. The minimum acceptable eye protection requires the use of hardened-glass or plastic safety spectacles.

Safety glasses used in the laboratory should comply with the Standard for Occupational and Educational Eye and Face Protection established by the American National Standards Institute. This standard specifies a minimum lens thickness of 3 mm, impact resistance requirements, passage of a flammability test, and lens-retaining frames.

Side shields that attach to regular safety spectacles offer some protection from objects that approach from the side but do not provide adequate protection from splashes. Other eye protection should be worn when a significant splash hazard exists.

OTHER EYE PROTECTION

It is important that each operation be analyzed to ensure that adequate eye protection is used. When operations that involve potential hazard to the eyes are performed (such as handling unusually corrosive chemicals), more complete eye protection than spectacles should be worn. It is the responsibility of the laboratory custodian to determine the level of eye protection required and to enforce eye protection rules.

Other forms of eye protection that may be required for a particular operation include the following:

Goggles: Goggles are not intended for general use. They are intended for wear when there is danger of splashing chemicals or flying particles. For example, goggles should be worn when working with glassware under reduced or elevated pressure and when glass apparatus is used in combustion or other high temperature operations. Impact protection goggles have screened areas on the sides to provide ventilation and reduce fogging of the lens and do not offer full protection against chemical splashes. Splash goggles (acid goggles) (or face shields) that have splash proof sides should be used when protection from harmful chemical splash is needed.

Face Shields: Goggles offer little protection to the face and neck. Full face shields that protect the face and throat should always be worn when maximum protection from flying particles and harmful liquids is needed; for full protection, safety glasses should be worn with face shields. The metal framed "nitrometer" mask offers greater protection for the head and throat from hazards such as flying glass or other light fragments. A face shield or mask may be needed when a vacuum system (which may implode) is used or when a reaction that has a potential for mild explosions is conducted.

Specialized Eye Protection: There are specific goggles and masks for protection against laser hazards ultraviolet or other intense light sources, as well as glassblowing goggles and welding masks and goggles. The laboratory custodian should determine whether the task being performed requires specialized eye protection and insist on the use of such equipment if it is necessary.

GLOVES

Skin contact is a potential source of Exposure to toxic materials; it is important that the proper steps be taken to prevent such contact.

1. Proper protective gloves (and other protective clothing, when necessary) should be worn whenever the potential for contact with corrosive or toxic materials and materials of unknown toxicity exists.
2. Gloves should be selected on the basis of the material being handled, the particular hazard involved, and their suitability for the operation being conducted.
3. Before each use, gloves should be inspected for discoloration, punctures, and tears.
4. Before removal, gloves should be washed appropriately. (NOTE: Some gloves, e.g., leather and polyvinyl alcohol, are water permeable.)
5. Glove materials are eventually permeated by chemicals. However, they can be used safely for limited time periods if specific use and glove characteristics (i.e., thickness and permeation rate and time) are known. Some of this information can be obtained from glove manufacturers, or the gloves used can be tested for breakthrough rates and times.
6. Gloves should be replaced periodically, depending on frequency of use and permeability to the substance(s) handled. Gloves overtly contaminated (if impermeable to water) should be rinsed and then carefully removed.

Gloves should be worn whenever it is necessary to handle corrosive materials, rough or sharp-edged objects, very hot or very cold materials, or whenever protection is needed against accidental exposure to chemicals. Gloves should not be worn around moving machinery. Many different types of gloves are commercially available.

1. Leather gloves may be used for handling broken glassware, for inserting glass tubes into rubber stoppers, and for similar operations where protection from chemicals is not needed.
2. There are various compositions and thicknesses of rubber gloves. Common glove materials include neoprene, polyvinyl chloride, nitrile, and butyl and natural rubbers. These materials differ in their resistance to various substances. Specific information on this topic is often available from glove manufacturers' catalogs, although such data are usually only qualitative; an example of information is given in Table III.1. Rubber gloves should be inspected before each use; periodically, an inflation test, in which the glove is first inflated with air and then immersed in water and examined for the presence of air bubbles, should be conducted.
3. Insulated gloves should be used when working at temperature extremes. Various synthetic materials such as Nomex and Kevlar can be used briefly up to 1000 °F. Gloves made with these materials or in combination with other materials such as leather are available. It is best not to use gloves made either entirely or partly of asbestos, which is regulated as a carcinogen under OSHA, although such gloves probably do not present a great hazard.
4. Specialized gloves are manufactured for electrical linesmen, welders, and others. It is the responsibility of the laboratory custodian to determine whether specialized hand protection is needed for any operation and to ensure that needed protection is available.

TABLE III.1 Resistance to Chemicals of Common Glove Materials
(E = Excellent, G = Good, F = Fair, P = Poor)

Chemical	Natural Rubber	Neoprene	Nitrile	Vinyl
Acetaldehyde	G	G	E	G
Acetic acid	E	E	E	E
Acetone	G	G	G	F
Acrylonitrile	P	G	--	F
Ammonium hydroxide (sat)	G	E	E	E
Aniline	F	G	E	G
Benzaldehyde	F	F	E	G
Benzene ^a	P	F	G	F
Benzyl chloride ^a	F	P	G	P
Bromine	G	G	--	G
Butane	P	E	--	P
Butyraldehyde	P	G	--	G
Calcium hypochlorite	P	G	G	G
Carbon disulfide	P	P	G	F
Carbon tetrachloride ^a	P	F	G	F
Chlorine	G	G	--	G
Chloroacetone	F	E	--	P
Chloroform ^a	P	F	G	P
Chromic acid	P	F	F	E
Cyclohexane	F	E	--	P
Dibenzyl ether	F	G	--	P
Dibutyl phthalate	F	G	--	P
Diethanolamine	F	E	--	E
Diethyl ether	F	G	E	P
Dimethyl sulfoxide ^b				
Ethyl acetate	F	G	G	F
Ethylene dichloride ^a	P	F	G	P
Ethylene glycol	G	G	E	E
Ethylene trichloride ^a	P	P	--	P
Fluorine	G	G	--	G
Formaldehyde	G	E	E	E
Formic acid	G	E	E	E
Glycerol	G	G	E	E
Hexane	P	E	--	P
Hydrobromic acid (40%)	G	E	--	E

Hydrochloric acid (conc)		G		G		G		E
Hydrofluoric acid (30%)	G		G		G		E	
Hydrogen peroxide	G		G		G		E	

TABLE III.1 (cont.) Resistance to Chemicals of Common Glove Materials

(E = Excellent, G = Good, F = Fair, P = Poor)

Chemical	Natural Rubber	Neoprene	Nitrile	Vinyl	
Iodine	G	G	--	G	
Methylamine	G	G	E	E	
Methyl cellosolve	F	E	--	P	
Methyl chloride ^a		P	E	--	P
Methyl ethyl ketone	F	G	G	P	
Methylene chloride ^a	F	F	G	F	
Monoethanolamine	F	E	--	E	
Morpholine	F	E	--	E	
Naphthalene ^a	G	G	E	G	
Nitric acid (conc)	P	P	P	G	
Perchloric acid	F	G	F	E	
Phenol	G	E	--	E	
Phosphoric acid	G	E	--	E	
Potassium hydroxide (sat)	G	G	G	E	
Propylene dichloride ^a	P	F	--	P	
Sodium hydroxide	G	G	G	E	
Sodium hypochlorite	G	P	F	G	
Sulfuric acid (conc)	G	G	F	G	
Toluene ^a	P	F	G	F	
Trichloroethylene ^a	P	F	G	F	
Tricresyl phosphate	P	F	--	F	
Triethanolamine		F	E	E	E
Trinitrotoluene	P	E	--	P	

- a) Aromatic and halogenated hydrocarbons will attack all types of natural and synthetic glove materials. Should swelling occur, the user should change to fresh gloves and allow the swollen gloves to dry and return to normal.

- b) No data on the resistance to dimethyl sulfoxide of natural rubber, neoprene, nitrile rubber, or vinyl materials are available; the manufacturer of the substance recommends the use of butyl rubber gloves.

OTHER CLOTHING AND FOOTWEAR

The clothing worn by laboratory workers can be important to their safety. Such personnel should not wear loose (e.g., saris, dangling neckties, and overlarge or ragged laboratory coats), skimpy (e.g., shorts and/or halter tops), or torn clothing and unrestrained long hair. Loose or torn clothing and unrestrained long hair can easily catch fire, dip into chemicals, or become ensnared in apparatus and moving machinery; skimpy clothing offers little protection to the skin in the event of chemical splash. If the possibility of chemical contamination exists, personal clothing that will be worn home should be covered by protective apparel.

Finger rings can react with chemicals and also should be avoided around equipment that has moving parts.

Shoes should be worn at all times in buildings where chemicals are stored or used. Perforated shoes, sandals, or cloth sneakers should not be worn in laboratories or areas where mechanical work is being done.

PROTECTIVE APPAREL

Appropriate protective apparel is advisable for most laboratory work and may be required for some. Such apparel can include laboratory coats and aprons, jump suits, special types of boots, shoe covers, and gauntlets. It must be either washable or disposable in nature. Garments are commercially available that can help protect the laboratory worker against chemical splashes or spills, heat, cold, moisture, and radiation.

Protective apparel should resist physical hazards and permit easy execution of manual tasks while being worn. It should also satisfy other performance requirements--strength, chemical and thermal resistance, flexibility, and ease of cleaning. The required degree of performance can be determined on the basis of the substances being handled. The choice of garment--laboratory coat versus rubber or plastic apron versus disposable jump suit--depends on the degree of protection required and is the responsibility of the laboratory custodian.

Laboratory coats are intended to prevent contact with dirt and the minor chemical splashes or spills encountered in laboratory-scale work. The cloth laboratory coat is, however, primarily a protection for clothing and may itself present a hazard (e.g., combustibility) to the wearer; cotton and synthetic materials such as Nomex^R or Tyvek^R are satisfactory; rayon and polyesters are not. Laboratory coats do not significantly resist penetration by organic liquids and, if significantly contaminated by them, should be removed immediately.

Plastic or rubber aprons provide better protection from corrosive or irritating liquids but can complicate injuries in the event of fire. Furthermore, a plastic apron can accumulate a considerable charge of static electricity and should be avoided in areas where flammable solvents or other materials could be ignited by a static discharge. Disposable outer garments (e.g., Tyvek) may, in some cases, be preferable to reusable ones. One such case is that of handling appreciable quantities of known carcinogenic materials, for which long sleeves and the use of gloves are also recommended. Disposable full length jump suits are strongly recommended for high-risk situations, which may also require the use of head and shoe covers. Many disposable garments, however, offer only limited protection from vapor penetration and considerable judgment is needed when using them. Impervious suits fully enclosing the body may be necessary in emergency situations.

Laboratory workers should know the appropriate techniques for removing protective apparel, especially any that has become contaminated. Chemical spills on leather clothing or accessories (watchbands, shoes, belts, and such) can be especially hazardous because many chemicals can be absorbed in the leather and then held close to the skin for long periods. Such items must be removed promptly and decontaminated or discarded to prevent the possibility of chemical burn. Specialized or disposable clothing for use with particular classes of hazardous chemicals should be treated in a similar way. Safety showers should be readily accessible for use when a chemical spill contaminates large sections of clothing or skin.

FOOT PROTECTION

More extensive foot protection than ordinary shoes may be required in some cases. Rubber boots or plastic shoe covers may be used to avoid possible exposure of the feet to corrosive chemicals or large quantities of solvents and water that might penetrate normal foot gear (e.g., during cleanup operations). Because these types of boots and covers may increase the risk of static spark, their use in normal laboratory operations is not advisable.

Other specialized tasks may require footwear that has, for example, conductive soles, insulated soles, or built-in metal toe caps. The laboratory custodian should recommend the use of such protection whenever appropriate.

SAFETY EQUIPMENT

Safety and emergency equipment should be available in all laboratories. The protection afforded by this equipment depends on its proper and consistent use. Laboratory workers should realize that safety devices are intended to help protect them from injury and should not avoid using such devices when they are needed.

All laboratories in which chemicals are used should have available fire extinguishers, safety showers, and eyewash fountains, as well as laboratory hoods and laboratory sinks (which can be considered part of the safety equipment of the laboratory); Respiratory protection for emergency use should be available nearby, along with fire alarms, emergency telephones, and identified emergency telephone numbers.

In addition to these standard items, there may also be a need for other protection. It is the responsibility of the laboratory custodian to recommend and provide supplementary safety equipment as needed.

FUME HOODS

Although many laboratory workers regard fume hoods as local ventilation devices to be used to prevent toxic, offensive, or flammable vapors from entering the general laboratory atmosphere, hoods offer two other significant types of protection. Placing a reacting chemical system within a hood, especially with the hood sash closed, places a physical barrier between the workers in the laboratory and the chemical reaction. This barrier can afford the laboratory workers significant protection from hazards such as chemical splashes or sprays, fires, and minor explosions. Furthermore, the hood can provide an effective containment device for accidental spills of chemicals.

Although there are many types of fume hoods, there are common features to most of them. Fume Hoods may be classified based on their design and the intended application.

TYPES OF FUME HOODS

Conventional Fume Hood

This is a basic enclosure with a movable front sash and an interior baffle. The sash may be fully opened to accommodate a variety of apparatus inside the hood, and the baffle simply guides exhaust air to follow specific flow patterns within the hood. The performance of this hood is dependent on sash position. Closing the sash disrupts the air flow and results in high-velocity air passing through the sash opening, which can damage fragile apparatus or disturb instrumentation.

By-Pass Fume Hood

The by-pass air hood is quite similar to a conventional hood, except that it is designed to permit some exhaust air to "by-pass" the sash closure. This eliminates the basic drawback of the conventional hood. The by-pass air hood is more desirable for use with fragile apparatus and instrumentation since the face velocity does not reach levels which might be detrimental to experimentation.

Auxiliary (Make-Up) Air Fume Hood

The auxiliary air hood provides a means of introducing outside air to the hood exhaust and limits the percentage of tempered air removed from the laboratory. Usually, the auxiliary system supplies air downward across the sash and into the hood opening. The merits of such a system are debatable. The idea is that the auxiliary air should not have to be fully conditioned as room air. Auxiliary air supply systems may, or may not, incorporate the by-pass design.

SPECIAL PURPOSE FUME HOODS

Perchloric Acid Fume Hood

Due to the potential explosion hazard of perchloric acid when combined with organic materials, this hood type must be used for perchloric acid digestion. It must be constructed of relatively inert materials such as type 316 stainless steel, ceramic coated material, or PVC. Hoods used for these applications should have integral bottoms, covered interiors, and a drain. Wash down features are required since the hood and duct

system must be thoroughly rinsed after each use to prevent the accumulation of reactive residue. Perchloric acid hoods are by their nature, of the by-pass type.

Radioactive Fume Hood

Hoods used for radioactive applications should have integral bottoms and covered interiors to facilitate decontamination. These units should also be strong enough to support lead shielding bricks, in case they are required. These hoods are also of the by-pass type.

Face Velocity

The operation of a fume hood is significantly impacted by the air flow from the laboratory into the hood and within the hood. The objective is to assure that little or no gasses generated inside the hood are released into the laboratory. There is a consensus that the face velocity measured as linear foot per minute (LFPM) measured in front of the hood is a reasonable measure of hood performance.

There is no legal standard for operation of fume hoods. However, many organizations have provided recommendations. Table III.2 contains data for selected sources. Based on this data, a value of 80-120 LFPM appears to be a reasonable one.

TABLE III.2 Recommended Face Velocities

<u>Organization</u>	<u>Recommended Face Velocity (LFPM)</u>
ACGIH ¹	60 - 100
NIOSH ²	100 - 150
ANSI ³ Z9.2, 1971	100 - 150
OSHA ⁴	60 - 100
NRC ⁵ Reg. Guide 8.23	Radionuclides at medical facilities
California OSHA	100 minimum

¹ American Conference of Governmental Industrial Hygienists

² National Institute of Occupational Safety and Health, DHSS

³ American National Standard Institute

⁴ Occupational Safety and Health Administration

⁵ Nuclear Regulatory Commission

OPERATION OF FUME HOODS

The following factors should be considered in application of fume hoods:

1. Hoods should be considered as backup safety devices that can contain and exhaust toxic, offensive, or flammable materials when the design of an experiment fails and vapors or dusts escape from the apparatus being used. Hoods should not be regarded as means for disposing of chemicals.
2. Hoods should be evaluated before each use by laboratory personnel to ensure adequate face velocities (typically 80-120 linear foot per minute {LFPM}) and the absence of excessive turbulence. Further, some continuous monitoring device for adequate hood performance should be present and should be checked before the hood is used (i.e., swinging vane velometer).
3. Except when adjustments of apparatus within the hood are being made, the hood should be kept closed: vertical sashes down and horizontal sashes closed. Sliding sashes should not be removed from horizontal sliding-sash hoods. Keeping the face opening of the hood small improves the overall performance of the hood.
4. The airflow pattern, and thus the performance of a hood, depends on such factors as placement of equipment in the hood, room drafts from open doors or windows, persons walking by, or even the presence of the user in front of the hood. For example, the placement of equipment in the hood can have a dramatic effect on its performance. Moving an apparatus 5-10 cm back from the front edge into the hood can reduce the vapor concentration at the face by 90%.
5. Hoods are not intended for storage of chemicals. Materials stored in them should be kept to a minimum. Stored chemicals should not block vents or alter airflow patterns. Whenever practical, chemicals should be moved from hoods to storage cabinets.
6. Solid objects and materials (such as paper) should not be permitted to enter the exhaust ducts of hoods as they can lodge in the ducts or fans and adversely affect their operation.
7. An emergency plan should always be prepared for the event of a ventilation failure (i.e., power failure or fan belt breakage) or other unexpected occurrence such as fire or explosion in the hood.
8. Fume hoods should be checked annually to ensure that they are in proper working order.

IV. PROCEDURES FOR ORDERING AND PROCUREMENT OF CHEMICALS

The achievement of safe handling, use, and disposal of hazardous substances begins with the persons who requisition such substances and those who approve their purchase orders. These persons must be aware of the potential hazards of the substances being ordered, know whether or not adequate facilities and trained personnel are available to handle such substances, and should ensure that a safe disposal route exists.

Before a new substance that is known or suspected to be hazardous is received, information concerning its proper handling methods, including proper disposal procedures, should be given to all those who will be involved with it. It is the responsibility of the laboratory custodian to ensure that the facilities are adequate and that those who will handle any material have received proper training and education to do so safely.

Material Safety Data Sheets provide physical property data and toxicological information, can be obtained by request to the EHS. However, the quality and depth of information on these sheets varies widely. For substances for which such sheets are not available, e.g., research chemicals usually sold in small quantities, the manufacturer, if contacted directly, will usually provide whatever health and safety information is available. The U.S. Department of Transportation (DOT) requires that shippers furnish and attach department-prescribed labels on all shipments of hazardous substances. These labels indicate the nature of the hazard of the substance shipped and thus provide some indication to the recipient of the type of hazard received, but should not be relied on after the container has been opened.

Because storage in laboratories is usually restricted to small containers, it is sometimes preferable to order in small-container lots to avoid the hazards associated with repackaging. Some chemical suppliers ship solvents in small metal containers to avoid the hazard of breakage.

Most investigators believe that ordering large quantities of solvents and chemicals would save money. This opinion is based on the cost of obtaining those materials on large quantity discounts offered by the suppliers. In many cases, this assumption overlooks the cost of disposal of unused chemicals. It should be remembered that often it is more expensive to dispose of a chemical than to buy it. Although the cost of the disposal is commonly not charged to the investigator, the University pays for the disposal and eventually this cost is reflected in the overhead.

As a general rule, chemicals should be purchased to be used within one week of arrival and certainly no longer than one month of arrival.

V. PROCEDURES FOR STORING CHEMICALS IN STORAGE AREAS

There is a range of possibilities for storing chemical substances. The arrangements made will depend on the size of the organization, the quantities handled, and the nature of the problems.

Often, the provision of adequate storage space is given little consideration in the design of laboratory buildings. Lack of sufficient storage space can create hazards due to overcrowding, storage of incompatible chemicals together, and poor housekeeping. Adequate, properly designed and ventilated storage facilities should be provided to ensure personnel safety and property protection.

In many instances, chemicals are delivered directly to the individual who initiated the order. If the facilities of the laboratory are appropriate for the kinds and quantities of materials used, this system may be eminently satisfactory. However, experience has shown that it is sometimes necessary to maintain a reserve of supplies in excess of the amounts that can be kept safely in the laboratory. If the quantities are large or the volumes of the individual containers are such that repackaging is necessary, then a safe place is needed to store these containers and to perform these functions. Depending on needs, this could be a stock room for the laboratory.

Stored chemicals should be examined at periodic intervals (at least quarterly). At this time, those that have been kept beyond their appropriate shelf life or have deteriorated, have questionable labels, are leaking, have corroded caps, or have developed any other problem should be disposed off in a safe manner.

A first-in, first-out system of stock keeping should be used. Shelved chemicals can walk, creep, and even tip over. Such chemicals can be prevented from falling off by placing retaining shock cords or similar restraining devices across the open face of the shelf or by raising the forward face of the shelf about one-quarter inch.

STOCKROOM DESIGN

Stockrooms should be usually within or close to the areas served. Stockrooms should not be used as preparation areas because of the possibility that an accident will occur and thereby unnecessarily contaminate a large quantity of materials. Preparation and repackaging should be performed in a separate area.

Stockrooms should be conveniently located and open during normal working hours so that laboratory workers need not store excessive quantities of chemicals in their laboratories. However, this does not imply that all laboratory workers should have unlimited access to the chemicals in the stockroom. Procedures must be established for the operation of any stockroom that place responsibility for its safety and inventory control in the hands of one person. At Temple University, this individual is the custodian of the stockroom, who must be readily available.

Stockrooms should be well ventilated. If storage of opened containers is permitted, extra local exhaust ventilation and the use of outside storage containers or spill trays are necessary.

FLAMMABLE LIQUIDS

At Temple University, the storage of bulk quantities of flammable materials is discouraged. However, if needed, centralized storage of bulk quantities of flammable liquids provides the best method of controlling the associated fire hazard.

Because the most effective way to minimize the impact of a hazard is to isolate it, a storage and dispensing room for flammable liquids is best located in a special building separated from the main building. If this is not reasonable, and the room must be located in a main building, the preferred location is a cutoff area on the at-grade level and having at least one exterior wall. Cutoff is a fire-protection term defined as "separated from other areas by fire-rated construction." In any case, storage rooms for flammable liquids should not be placed on the roof, located on a below-grade level, an upper floor, or in the center of the building. All of these locations are undesirable because they are less accessible for fire fighting and potentially dangerous to the safety of the personnel in the building.

The walls, ceilings, and floors of an inside storage room for flammable liquids should be constructed of materials having at least a 2-hour fire resistance, and there should be self-closing Class B fire doors. All storage rooms should have adequate mechanical ventilation controlled by a switch outside the door and explosion-proof lighting and switches. Other potential sources of ignition, such as burning tobacco and lighted matches, should be forbidden.

DRUM STORAGE

Occasionally, 55 gallon drums are used to ship flammable liquids but are not intended as long-time inside storage containers. It is not safe to dispense from sealed drums exactly as they are received. The bung should be removed and replaced by an approved pressure and vacuum relief vent to protect against internal pressure buildup in the event of fire or if the drum might be exposed to direct sunlight.

If possible, drums should be stored on metal racks placed such that the end bung openings are toward an aisle and the side bung openings are on top. The drums, as well as the racks, should be grounded with a minimum length of American wire gage 10 wire. Because effective grounding requires metal-to-metal contact, all dirt, paint, and corrosion must be removed from the contact areas. Spring-type battery clamps and a minimally sized conductor (e.g., American wire gage 8 or 10) are satisfactory. It is also necessary to provide bonding to metal receiving containers to prevent accumulation of static electricity (which will discharge to the ground, creating a spark that could ignite the flammable vapors). Drip pans that have flame arresters should be installed or placed under faucets.

Dispensing from drums is usually done by one of two methods. The first is gravity based through drum faucets that are self-closing and require constant hand pressure for operation. Faucets of plastic construction are not generally acceptable due to chemical action on the plastic materials. The second, and safer, method is to use an approved hand-operated rotary transfer pump. Such pumps have metering options and permit immediate cutoff control to prevent overflow and spillage, can be reversed to siphon off excess liquid in case of overfilling, and can be equipped with drip returns so that any excess liquid can be returned to the drum.

TOXIC SUBSTANCES

Toxic substances should be segregated from other substances and stored in a well-defined or identified area that is cool, well ventilated, and away from light, heat, acids, oxidizing agents, moisture, and such.

The storage of unopened containers of toxic substances normally presents no unusual requirements. However, because containers occasionally develop leaks or are broken, storage rooms should be equipped

with exhaust hoods or equivalent local ventilation devices in which containers of toxic substances can be handled.

Opened containers of toxic substances should be closed with tape or other sealant before being returned to the storeroom and should not be returned unless some type of local exhaust ventilation is available.

WATER-SENSITIVE CHEMICALS

Some chemicals react with water to evolve heat and flammable or explosive gases. For example, potassium and sodium metals and many metal hydrides react on contact with water to produce hydrogen, and these reactions evolve sufficient heat to ignite the hydrogen with explosive violence. Certain polymerization catalysts, such as aluminum alkyls, react and burn violently on contact with water.

Storage facilities for water-sensitive chemicals should be constructed to prevent their accidental contact with water. This is best accomplished by eliminating all sources of water in the storage area; for example, areas where large quantities of water-sensitive chemicals are stored should not have automatic sprinkler systems. Storage facilities for such chemicals should be of fire-resistant construction, and other combustible materials should not be stored in the same area.

DISTRIBUTING OF CHEMICALS

The method of transport of chemicals between storage areas and laboratories must reflect the potential danger posed by the specific substance.

When chemicals are hand carried, they should be placed in an outside container or acid-carrying bucket to protect against breakage and spillage. When they are transported on a wheeled cart, the cart should be stable under the load and have wheels large enough to negotiate uneven surfaces (such as expansion joints and floor drain depressions) without tipping or stopping suddenly.

To avoid exposure to persons on passenger elevators, if possible, chemicals should be transported on freight-only elevators. Provisions for the safe transport of small quantities of flammable liquids include (a) the use of rugged pressure-resistant, non-venting containers, (b) storage during transport in a well-ventilated vehicle, and (c) elimination of potential ignition sources.

COMPRESSED GASES

Cylinders of compressed gases should be stored in well-ventilated, dry areas. Where practicable, storage rooms should be of fire-resistant construction and above ground. Cylinders may be stored out of doors, but some protection must be provided to prevent corrosion of the cylinder bottom and air circulation must not be restricted.

Compressed gas cylinders should not be stored near sources of ignition nor where they might be exposed to corrosive chemicals or vapors. They should not be stored where heavy objects might strike or fall on them, such as near elevators, service corridors, and unprotected platform edges. The cylinder storage area should be posted with the names of the gases stored. Where gases of different types are stored at the same location, the cylinders should be grouped by type of gas (e.g., flammable, toxic, or corrosive). If possible,

however, flammable gases should be stored separately from other gases and provision should be made to protect them from fire. Full and empty cylinders should be stored in separate portions of the storage area, and the layout should be arranged so that older stock can be used first with minimum handling of other cylinders.

Cylinders and valves are usually equipped with various safety devices, including a fusible metal plug that melts at 70-95°C. Although most cylinders are designed for safe use up to a temperature of 50°C, they should not be placed where they can become overheated (e.g., near radiators, steam pipes, or boilers). Cylinder caps to protect the container withdrawal valve should be in place at all times during storage and movement to and from storage. Cylinders should be stored in an upright position where they are unlikely to be knocked over, or they should be secured in an upright or horizontal position. Acetylene cylinders should always be stored valve end up to minimize the possibility of discharge. Oxygen should be stored in an area that is at least 20 ft away from any flammable or combustible materials (especially oil and grease) or separated from them by a noncombustible barrier at least 5 ft high and having a fire resistance rating of at least 1/2 hour.

Cylinders are sometimes painted by the vendor to aid in the recognition of their contents and make separation of them during handling easier. However, this color coding is not a reliable method for identification of their contents; the stenciled or printed name on the cylinder is the only accepted method. If it is suspected that the stored cylinder is leaking, the procedures described in Section II.E.6 should be followed. The cylinders that contain compressed gases are primarily shipping containers and should not be subjected to rough handling or abuse. Such misuse can seriously weaken the cylinder and render it unfit for further use or transform it into a rocket having sufficient thrust to drive it through masonry walls. To protect the valve during transportation, the cover cap should be left screwed on hand tight until the cylinder is in place and ready for actual use. Cylinders should never be rolled or dragged. The preferred transport, even for short distances, is by suitable hand truck with the cylinder strapped in place. Only one cylinder should be handled at a time.

VI. PROCEDURES FOR STORING CHEMICALS IN LABORATORIES

The amounts of toxic, flammable, unstable, or highly reactive materials that should be permitted in laboratories are an important concern. To arbitrarily restrict quantities may interfere with laboratory operations but, conversely, unrestricted quantities can result in the undesirable accumulation of such materials in the laboratory.

It is necessary to balance the needs of the laboratory workers and the established requirements for safety. Decisions in this area will be affected by the level of competence of the workers, the level of safety features designed into the facility, the location of the laboratory, the nature of the chemical operations, and the accessibility of the stockroom. In general, all laboratories should have two exits (one that may be an emergency exit) so that a fire at one exit will not block occupants' escape; doors that open outward are desirable.

GENERAL CONSIDERATIONS

Every chemical in the laboratory should have a definite storage place and should be returned to that location after each use.

The storage of chemicals on bench tops is undesirable; in such locations, they are unprotected from potential exposure to fire and are also more readily knocked over. Storage in hoods is also inadvisable because this practice interferes with the air flow in the hood, clutters up the working space, and increases the amount of materials that could become involved in a hood fire.

Storage trays or secondary containers should be used to minimize the distribution of material should a container break or leak. Because most laboratory workers tend to store hazardous materials in the cabinet space under the hood, the provision of ventilated cabinets in this location is advisable. The use of such cabinets also has the advantage that, because of proximity to the hood, the safe practice of making transfers of hazardous materials in the hood is encouraged.

Care should be taken to avoid exposure of chemicals to heat or direct sunlight and to observe precautions regarding the proximity of incompatible substances. Laboratory refrigerators are to be used for the storage of chemicals only; food must not be placed in them. All containers placed in the refrigerator should be properly labeled (identification of contents and owner, date of acquisition or preparation, and nature of any potential hazard) and, if necessary, should be sealed to prevent escape of any corrosive vapors. Flammable liquids should not be stored in laboratory refrigerators unless the unit is an approved, explosion-proof, or laboratory-safe type (NFPA Standards 45 and 56D).

The chemicals stored in the laboratory should be inventoried periodically, and unneeded items should be given to EHS for recycling or disposal. At the same time, containers that have illegible labels and chemicals that appear to have deteriorated should be disposed of. On termination, transfer, graduation, or such of any laboratory personnel, those personnel and the laboratory custodian should arrange for transfer to EHS of all hazardous materials those persons have on hand.

FLAMMABLE LIQUIDS

OSHA regulations for the laboratory storage of flammable and combustible liquids are not based on fire prevention and protection principles but rather address the types and sizes of containers allowable. For example, OSHA would permit the storage of 60-gal metal drums in laboratories of colleges and universities. The NFPA standard (No. 45), on the other hand, has a quantity limit per 100 ft² that depends on the construction and fire protection afforded in the laboratory and restricts instructional laboratories to half the quantities for industrial or graduate student laboratories. A second NFPA standard (No. 30) addresses the amounts that may be stored outside of an approved flammable-liquid storage room or cabinet, but does not consider fire protection features available.

Whenever feasible, quantities of flammable liquids greater than 1 liter should be stored in metal containers.

Portable approved safety cans are one of the safest methods of storing flammable liquids. These cans are available in a variety of sizes and materials. They have spring-loaded spout covers that can open to relieve internal pressure when subjected to a fire and will prevent leakage if tipped over. Some are equipped with a flame arrester in the spout that will prevent flame propagation into the can. If possible, flammable liquids received in large containers should be repackaged into safety cans for distribution to laboratories. Such cans must be properly labeled to identify their contents.

Small quantities of flammable liquids should be stored in ventilated storage cabinets made of 18-gage steel and having riveted and spot-welded seams. Such cabinets are of double-wall construction and have a 1-in. air space between the inner and the outer walls. The door is 2 in. above the bottom of the cabinet, and the cabinet is liquid tight to this point. It is provided with vapor-venting provisions and can be equipped with a sprinkler system. (Materials that react with water should not be stored in sprinkler-equipped cabinets.) Some models have doors that close automatically in the event of fire. If, for reasons of cost or space limitations, storage cabinets must be constructed of wood, they should be built according to the Los Angeles Fire Department specifications (see also NFPA Standard 30).

In any case, the hazard of storage of flammable materials in wooden cabinets in existing laboratories can be decreased by the use of intumescent fire-retardant coatings or other means that provide effective fire insulation. [NOTE: On heating, intumescent materials expand from a thin paint-like coating to a thick puffy coating that insulates or excludes oxygen and protects the subsurface from ignition.] Other considerations in the storage of flammable liquids in the laboratory include ensuring that aisles and exits are not blocked in the event of fire; that accidental contact with strong oxidizing agents such as chromic acid, permanganates, chlorates, perchlorates, and peroxides is not possible; and that sources of ignition are excluded.

TOXIC SUBSTANCES

Chemicals known to be highly toxic, including those classified as carcinogens, should be stored in ventilated storage areas in unbreakable chemically resistant secondary containers.

TABLE VI.1 Container Size Limitations For Flammable and Combustible Liquids

Type of Container	Flammable Liquids					Combustible Liquids				
	Class II	Class IA		Class IB		Class IC		Liters	Gal	
		Class IIIA	Liters	Gal	Liters	Gal	Liters			Gal
Glass	0.5	0.12	1	0.25	4	1	4	1	4 ^a	1 ^a
Metal (other than DOT drums)	4	1	20	5	20	5	20	5	20	5
Safety cans	7.5	2	20	5	20	5	20	5	20	5
Metal drums (DOT specifications ^b) 60		225	60	225	60	225	60	225	60	225
Approved portable tanks ^c 660		2500	660	2500	660	2500	660	2500	660	2500

^aOSHA limitation; NFPA Nos. 30 and 45 allow 20 liters (5 gal).

^bMaximum size permitted in a laboratory for Class I materials is 20 liters (5gal); drum size is permitted only in an inside storage room (OSHA) (1910.106 and NFPA No. 30).

^cPermitted only outside of buildings.

Only minimum working quantities of toxic materials should be present in the work area. Storage vessels containing such substances should carry a label such as the following: CAUTION: HIGH CHRONIC TOXICITY or CANCER-SUSPECT AGENT.

Storage areas for substances that have high acute or chronic toxicity should exhibit a sign warning of the hazard, have limited access, and be adequately ventilated. Adequate ventilation is of particular concern for hazardous materials that have a high vapor pressure (such as bromine, mercury, and mercaptan).

COMPRESSED GASES

Cylinders of compressed gases should be securely strapped or chained to a wall or bench top to prevent their being knocked over accidentally. When they are not in use, it is good practice to keep them capped. Care should be taken to keep them away from sources of heat or ignition.

VII. INCOMPATIBLE CHEMICALS

The term "incompatible chemicals" refers to chemicals that can react with others

- Violently
- With evolution of substantial heat
- To produce flammable products or
- To produce toxic products.

The EPA RCRA regulations specify that incompatible chemicals must not be placed in the same lab pack for landfill disposal, and the DOT regulations have a similar proscription on packing incompatible chemicals for transport. Incompatible chemicals should always be handled, stored, and packed so that they cannot accidentally come into contact with each other.

Guidelines for the segregation of common laboratory chemicals that are incompatible are presented in Tables VII.1 and VII.2. Table VII.1 contains general classes of compounds that should be kept separated; Table VII.2 lists specific compounds that can pose reactivity hazards. Chemicals in each grouping in columns A and B of each table should be kept separate.

TABLE VII.1 General Classes of Incompatible Chemicals

A	B
Acids	Bases, metals
<i>Oxidizing Agents^a</i>	<i>Reducing agents^a</i>
Chlorates	Ammonia, anhydrous and
aqueous	
Chromates	Carbon
Chromium trioxide	Metals
Dichromates	Metal hydrides
Halogens	Nitrites
Halogenating agents	Organic compounds
Hydrogen peroxide	Phosphorus
Nitric acid	Silicon
Nitrates	Sulfur
Perchlorates	
Peroxides	
Permanganates	
Persulfates	

^aThe examples of oxidizing and reducing agents are illustrative of common laboratory chemicals; they are not intended to be exhaustive.

TABLE VII.2 Specific Chemical Incompatibilities

A	B
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Acetylene monosubstituted acetylenes (RC=CH)	and	Group 1B and IIB metals and salts Halogens Halogenating agents
Ammonia, anhydrous aqueous	and	Halogens Halogenating agents Mercury Silver
Alkali and alkaline earth carbides hydrides hydroxides metals oxides peroxides	}	Water Acids Halogenated organic compounds Halogenating agents Oxidizing agents
Azides, inorganic	}	Acids Heavy metals and their salts Oxidizing agents
Cyanides, inorganic	}	Acids Strong bases
Mercury and its amalgams	}	Acetylene Ammonia, anhydrous and aqueous Nitric acid Sodium azide
Nitrates, inorganic	}	Acids Reducing agents
Nitric acid	{ }	Bases Chromic acid Chromates Metals Permanganates Reducing agents Sulfides Sulfuric acid
Nitrites, inorganic	}	Acids Oxidizing agents
Organic compounds Organic acyl halides Organic anhydrides Organic halogens	{ }	Oxidizing agents Bases Organic hydroxy and amino compounds Bases Organic hydroxy and amino compounds Group IA and IIA metals Aluminum

Organic nitro compounds	Strong bases
	{ Mercury and its salts Silver and its salts
Oxalic acid	
	{ Oxidizing agents Oxygen Strong bases
Phosphorus	
	{ Alcohols Strong bases Water
Phosphorus pentoxide	
	{ Acids
Sulfides, inorganic	Bases, Potassium Permanganate, Water
Sulfuric acid (concentrated)	

VIII. POTENTIALLY EXPLOSIVE CHEMICALS AND REAGENT COMBINATIONS

Table VIII.1 lists some common classes of laboratory chemicals that have potential for producing a violent explosion when subjected to shock or friction. These chemicals should never be disposed of as such but should be handled by appropriate procedures.

TABLE VIII.1 Shock-Sensitive Compounds

Acetylenic compounds, especially polyacetylenes, haloacetylenes, and heavy metal salts of acetylenes (copper, silver, and mercury salts are particularly sensitive)

Acyl nitrates

Alkyl nitrates, particularly polyol nitrates such as nitrocellulose and nitroglycerin

Alkyl and acyl nitrites

Alkyl perchlorates

Amminemetal oxosalts: metal compounds with coordinated amonia, hydrazine, or similar nitrogenous donors and ionic perchlorate, nitrate, permanganate, or other oxidizing group

Azides, including metal, nonmetal, and organic azides

Chlorite salts of metals, such as AgClO_2 and $\text{Hg}(\text{ClO}_2)_2$

Diazo compounds such as CH_2N_2

Diazonium salts, when dry

Fulminates (silver fulminate, AgCNO , can form in the reaction mixture from the Tollens' test for aldehydes if it is allowed to stand for some time; this can be prevented by adding dilute nitric acid to the test mixture as soon as the test has been completed)

Hydrogen peroxide becomes increasingly treacherous as the concentration rises above 30%, forming explosive mixtures with organic materials and decomposing violently in the presence of transition metals

N-Halogen compounds such as difluoroamino compounds and halogen azides

N-Nitro compounds such as N-nitromethylamine, nitrourea, nitroguanidine, and nitric amide

Oxo salts of nitrogenous bases: perchlorates, dichromates, nitrates, iodates, chlorites, chlorates, and permanganates of ammonia, amines, hydroxylamne, guanidine, etc.

Perchlorate salts. Most metal, nonmetal, and amine perchlorates can be detonated and may undergo violent reaction in contact with combustible materials

Peroxides and hydroperoxides, organic

Peroxides (solid) that crystallize from or are left from evaporation of peroxidizable solvents

Peroxides, transition-metal salts

Picrates, especially salts of transition and heavy metals, such as Ni, Pb, Hg, Cu, and Zn; picric acid is explosive but is less sensitive to shock or friction than its metal salts and is relatively as a water-wet paste

Polynitroalkyl compounds such as tetranitromethane and dinitroacetonitrile

Polynitroaromatic compounds, especially polynitro hydrocarbons, phenols, and amines

Table VIII.2 lists a few illustrative combinations of common laboratory reagents that can produce explosions when they are brought together or that give reaction products that can explode without any apparent external initiating action. This list is by no means exhaustive; additional information of potentially explosive reagent combinations can be found in publications of the National Fire Protection Association.

TABLE VIII.2 Potentially Explosive Combinations of Some Common Reagents

Acetone + chloroform in the presence of base
Acetylene + copper, silver, mercury, or their salts
Ammonia (including aqueous solutions) Cl_2 , Br_2 , or I_2
Carbon disulfine + sodium azide
Chlorine + an alcohol
Chloroform or carbon tetrachloride + powdered Al or Mg
Decolorizing carbon + an oxidizing agent
Diethyl ether + chlorine (including a chlorine atmosphere)
Dimethyl sulfoxide + an acyl halide, SOCl_2 , or POCl_3
Dimethyl sulfoxide + CrO_3
Ethanol + calcium hypochlorite
Ethanol + silver nitrate
Nitric acid + acetic anhydride or acetic acid
Picric acid + a heavy-metal, such as a Pb, Hg, or Ag
Silver oxide + ammonia + ethanol
Sodium + a chlorinated hydrocarbon
Sodium hypochlorite + an amine

SODIUM AZIDE

Sodium azide, a bactericide widely used in medical research, represents a risk due to the possible formation of explosive azides with copper, lead and other heavy metals. Several explosions have been documented where sodium azide solutions had been used in laboratory equipment or discarded in waste water piping systems. These explosions usually occurred when service personnel applied heat or friction to azide contaminated metallic surfaces.

Heavy metal azides are highly explosive and are formed whenever sodium azide is allowed to react with metals such as lead or copper. The formation of metallic azides in sewer systems is thought to result when water combines with azide leading to the formation of hydrazoic acid (HN_3). Hydrazoic acid, itself an explosive, is then able to react with lead or copper to form highly explosive metallic azides.

To prevent azide formation, the following actions should be considered:

Substitution - Several commercial antibacterial products are available which do not use sodium azide (Clear-Bath, Roccal, etc.).

Flushing of Drains - Always flush drains or metallic equipment thoroughly after discarding sodium azide solutions. This may not eliminate the formation of azide compounds, but will reduce their amount.

Storage - Sodium azide solutions should not be stored in cabinets or refrigerators with exposed copper or lead parts.

Decontamination - Decontamination should be performed prior to repair or discard of all sodium azide contaminated metallic components or equipment. The decontamination process is as follows:

1. Make a dilute (2-10%) solution of NaOH
2. Pour the NaOH solution into the drain or equipment so as to flush all contaminated surfaces.
3. Treated materials should remain undisturbed for at least 16 hours.
4. Repeat two more times at intervals of one week.

Labelling - All drain lines or metallic equipment that are regularly exposed to sodium azide solutions should be labelled indicating the existence of potential explosion hazard. Labels are available from EHS.

IX. WATER-REACTIVE AND PYROPHORIC CHEMICALS

The following list contains some common laboratory chemicals that react violently with water and that should always be stored and handled so that they do not come into contact with liquid water or water vapor. They are prohibited from landfill disposal, even in a lab pack, because of the characteristic of reactivity.

Alkali metals
Alkali metal hydrides
Alkali metal amides
Metal alkyls, such as lithium alkyls and aluminum alkyls
Grignard reagents
Halides of nonmetals, such as BCl_3 , BF_3 , PCl_3 , PCl_5 , SiCl_4 , S_2Cl_2
Inorganic acid halides, such as POCl_3 , SOCl_2 , SO_2Cl_2
Anhydrous metal halides, such as AlCl_3 , TiCl_4 , ZrCl_4 , SnCl_4
Phosphorus pentoxide
Calcium carbide
Organic acid halides and anhydrides of low molecular weight

PYROPHORIC CHEMICALS

Many members of the following readily oxidized classes of common laboratory chemicals ignite spontaneously in air. Pyrophoric chemicals should be stored in tightly closed containers under an inert atmosphere (or, for some, an inert liquid), and all transfers and manipulations of them must be carried out under an inert atmosphere or liquid.

Grignard reagents, RMgX
Metal alkyls and aryls, such as RLi , RNa , R_3Al , R_2Zn
Metal carbonyls, such as $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Co}_2(\text{CO})_8$
Alkali metals such as Na, K
Metal powders, such as Al, Co, Fe, Mg, Mn, Pd, Pt, Ti, Sn, Zn, Zr
Metal hydrides, such as NaH , LiAlH_4
Nonmetal hydrides, such as B_2H_6 and other boranes, PH_3 , AsH_3
Nonmetal alkyls, such as R^3B , R_3P , R_3As
Phosphorus (white)

X. PEROXIDE-FORMING CHEMICALS

Many common laboratory chemicals can form peroxides when allowed access to air over a period of time. A single opening of a container to remove some of the contents can introduce enough air for peroxide formation to occur. Some types of compounds form peroxides that are treacherously and violently explosive in concentrated solution or as solids. Accordingly, peroxide-containing liquids should never be evaporated to dryness. Peroxide formation can also occur in many polymerizable unsaturated compounds, and these peroxides can initiate a runaway, sometimes explosive polymerization reaction.

This section provides a list of structural characteristics in organic compounds that can peroxidize and some common inorganic materials that form peroxides. Although the tabulation of organic structures may seem to include a large fraction of the common organic chemicals, they are listed in an approximate order of decreasing hazard. Reports of serious incidents involving the last five organic structural types are extremely rare, but they are included because laboratory workers should be aware that they can form peroxides that can influence the course of experiments in which they are used.

This section also provides specific examples of common chemicals that can become serious hazards because of peroxide formation. Suggested time limits are given for retention or testing of these compounds after opening the original container. Although some laboratories mark containers of such chemicals with the date of receipt of the original container, it should be recognized that such dating does not take into account the unknown time span between original packaging of the chemical and its date of receipt. The date of opening the original container of a chemical that is a hazardous peroxide-former should always be marked on the container. Labels such as that illustrated below should be provided to all laboratory workers to affix to and date all samples of peroxide-forming reagents that they receive.

PEROXIDIZABLE COMPOUND

RECEIVED	OPENED
DATE _____	_____

**DISCARD OR TEST WITHIN 6 MONTHS
AFTER OPENING**

Table X.2 gives examples of common laboratory chemicals that are prone to form peroxides on exposure to air. The lists are not exhaustive, and analogous compounds that have any of the structural features given in Table X.1 should be tested for the presence of peroxides before being used as solvents or being distilled. The recommended retention times begin with the date of synthesis or of opening the original container.

TABLE X.1 Types of Chemicals That Are Prone To Form Peroxides

A. Organic Substances (in approximate order of decreasing hazard)

	H		
1.	C-O-	\ /	Ethers and Acetals with a hydrogen atom
2.	C=C-C	\ // / \	Olefines with allylic hydrogen atoms.
3.	C=C-	\ /	Chloroolifines and fluoroolifines
4.	CH ₂ =C	/	Vinylhalides, esters and ethers
5.	C=C-C=C	\ / / \	Dienes
6.	C=C-C=CH	\ /	Vinylacetelens with a hydrogen atom
7.	C-C=CH	\ /	Alkylacetelens with a hydrogen atom
8.	C-Ar	\ /	Alkylarenes that contain tertiary hydrogen atoms
9.	-C-H		Alkanes and cycloalkanes that contain tertiary
hydrogen atoms			
10.	C=C-CO ₂ R	\ /	Acrylates and methacrylates
11.	C-OH	\ /	Secondary alcohols
12.	-C-C	/ O 	Ketones that contain a hydrogen atom
13.	-C=O	H 	Aldehydes

14. $\begin{array}{c} \text{O} \\ | \quad / \\ -\text{C}-\text{N}-\text{C} \\ \backslash \end{array}$ Ureas, amides and lactams that have a hydrogen atom on a carbon atom attached to nitrogen

B. Inorganic Substances:

1. Alkali metals, especially potassium, rubidium and cesium
2. Metal amides
3. Organometallic compounds with a metal atom bonded to carbon
4. Metal Alkoxides.

TABLE X.2 Common Peroxide-Forming Chemicals

LIST A

Severe Peroxide Hazard on Storage with Exposure to Air

Discard within 3 months

- | | |
|---------------------------------------|---|
| ● Diisopropyl ether (isopropyl ether) | ● Sodium amide (sodamide) |
| ● Divinylacetylene (DVA) ^a | ● Vinylidene chloride (1,1-dichloroethylene) ^a |
| ● Potassium metal | |
| ● Potassium amide | |

LIST B

Peroxide Hazard on Concentration; Do Not Distill or Evaporate Without First Testing for the Presence of Peroxides

Discard or test for peroxides after 6 months

- | | |
|--|--|
| ● Acetaldehyde diethyl acetal (acetal) | ● Dicyclopentadiene |
| ● Cumene (isopropylbenzene) | ● Diethyl ether (ether) |
| ● Cyclopentene | ● Diethylene glycol dimethyl ether (diglyme) |
| ● Decalin (decahydronaphthalene) | ● Furan |
| ● Dioxane | ● Methylacetylene |
| ● Ethylene glycol dimethyl ether (glyme) | ● Methylcyclopentane |
| ● Ethylene glycol ether acetates | ● Methyl isobutyl ketone |
| ● Ethylene glycol monoethers (cellosolves) | ● Tetrahydrofuran (THF) |
| ● Diacetylene (butadiene) | ● Tetralin (tetrahydronaphthalene) |
| | ● Vinyl ethers ^a |

LIST C

Hazard of Rapid Polymerization Initiated by Internally Formed Peroxide^a

a. Normal Liquids; Discard or test for peroxides after 6 months^b

- Chloroprene (2-chloro-1,3-butadiene)^c
- Styrene

- Vinyl acetate
- Vinylpyridine

b. Normal Gases; Discard after 12 months^d

- Butadiene^c
- Tetrafluoroethylene (TFE)^c

- Vinylacetylene (MVA)^c
- Vinyl chloride

^aPolymerizable monomers should be stored with a polymerization inhibitor from which the monomer can be separated by distillation just before use.

^bAlthough common acrylic monomers such as acrylonitrile, acrylic acid, ethyl acrylate, and methyl methacrylate can form peroxides, they have not been reported to develop hazardous levels in normal use and storage.

^cThe hazard from peroxides in these compounds is substantially greater when they are stored in the liquid phase, and if so stored without an inhibitor they should be considered as in LIST A.

^dAlthough air will not enter a gas cylinder in which gases are stored under pressure, these gases are sometimes transferred from the original cylinder to another in the laboratory, and it is difficult to be sure that there is no residual air in the receiving cylinder. An inhibitor should be put into any such secondary cylinder before one of these gases is transferred into it; the supplier can suggest inhibitors to be used. The hazard posed by these gases is much greater if there is a liquid phase in such a secondary container, and even inhibited gases that have been put into a secondary container under conditions that create a liquid phase should be discarded within 12 months.